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UTILIZATION OF WASTE: EXPERIMENTAL PRODUCTION OF BRICKS FROM DICALCIUM SILICATE SLAG

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by

D. G. Feasby*

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SUMMARY OF RESULTS

Dicalcium silicate slag, (Ca_2SiO_4), is produced and discarded by an Ontario magnesium producer. Bricks were fabricated from this waste by screening, hydrating residual magnesium oxide, and steam-autoclaving dry-pressed shapes. The bricks were of acceptable quality for commercial use when the raw brick mix included 50 per cent by weight of filler such as clean sand. However, a preliminary economic analysis of a probable production scheme revealed that building elements made from this waste could not be economically produced and marketed at this time. Consideration could be given to the process in future years when increased energy costs may more adversely affect fired products, e.g., cement, lime, clay.

The slag was examined for agricultural uses and as a raw material for Portland-type cement production. Results showed that this material was not satisfactory for either of these purposes.

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UTILISATION DE RESIDU: PRODUCTION EXPERIMENTALE DE BRIQUES A PARTIR D'UNE SCORIE DE SILICATE DE DICALCIUM

par

D.G. Feasby*

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UN APERCU DES RESULTATS

Une scorie de silicate de dicalcium (Ca_2SiO_4) a été produite et rejetée par un producteur de magnésium ontarien. Des briques ont été fabriquées de ce résidu: premièrement la poudre de silicate a été tamisée, puis l'oxyde de magnésium résiduel a été hydraté pour enfin obtenir les briques pressées à sec à l'aide d'un autoclave à vapeur. La qualité des briques était satisfaisante pour une utilisation commerciale lorsque le mélange brut des briques contenait 50 pour cent au poids de remplissage,comme par exemple du sable propre. Toutefois, une anaiyse économique préliminaire d'un plan de production probable a révélé que des matériaux de construction faits à partir de ce résidu ne peuvent être produits et mis sur le marché de façon rentable par les temps qui courent. On pourra peut-être considéré le procédé dans les années à venir lorsque les coûts élevés de l'énergie effecteront les produits cuits comme le ciment, la chaux et l'argile.

La scorie a aussi été examinée pour des fins agricoles comme matériel brut dans la production de ciment de type Portland. Les résultats ont démontré que ce matériel n'est pas acceptable dans ni l'un ni l'autre des cas.

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CONTENTS

	Page
Summary of Results	i
Résumé des Résultats	ii
Contents	iii
Tables	iv
Figures	v
Introduction	1
The Slag	1
The Manufacture of Autoclaved Blocks with Waste Dicalcium Silicate Slag	8
Hydration of Residual Magnesia	8
Fabrication of Brick	15
A. Pressing	15
B. Autoclave Procedure	15
C. Specimen Testing	18
Results	18
A. Moulding Pressure and Autoclaving Time	18
B. Filler Additions	18
C. Autoclave Pressure and Time	21
D. Standard Tests	21
Economics of Brick Production	25
Conclusions	29
Acknowledgements	29
References	30
Appendix I, The Manufacture of Hydraulic Cement from Dicalcium Silicate Slag	
Appendix II, The Use of Dicalcium Silicate Slag in Agriculture	
Appendix III, Screen Analyses of Fillers Added to Slag for Bricks	

TABLES

No.		Page
1	Sieve Analyses of Dicalcium Silicate Slag, Wt Per Cent.....	3
2	Chemical Analyses of Dicalcium Silicate Slag Fractions (Air-Cooled) - Wt Per Cent.....	3
3	Quatitative X-ray Analyses of Dicalcium Silicate Slag.....	4
4	Hydraulic Activity of 50% Slag (-100 mesh), 50% Silica (-200 mesh) Mixture.....	4
5	Miscellaneous Properties of Dicalcium Silicate Slag.....	6
6	Hydration of Slag as Thick Slurry at 194°F (90°C), (60% solids)..	10
7	Hydration of Slag as Moist Powder in an Autoclave.....	11
8	Hydration of Slag as a Thick Slurry under Pressure, 50 Per Cent Solids, 50 psig (0.34 MPa).....	12
9	Summary of Slag Brick Properties.....	23
10	Estimated Capital Cost for Brick Production.....	27
11	Estimated Manufacturing Cost per 1,000 Bricks.....	28

FIGURES

No.		Page
1	Weight loss vs temperature for minus 100-mesh dicalcium silicate slag, as received, and after autoclaving for 24 hours....	7
2	Slag cylinders formed with minus 100-mesh material (left) and (right) after autoclaving at 392°F (200°C).....	9
3	"Half" bricks made from slag; magnesia incompletely hydrated (left), and completely hydrated (right).....	13
4	Change of surface area with autoclaving of screened slag.....	16
5	Fine particle size analyses of minus 200-mesh slag, as received, and autoclaved 24 hours at 50 psig (0.34 MPa).....	17
6	Effect of moulding pressure and autoclaving time on compressive strength of slag cylinders.....	19
7	Effect of various fillers on the compressive strength of slag cylinders autoclaved for 48 hours at 100 psig (0.69 MPa).....	20
8	Effect of autoclaving time and pressure on the compressive strength of sand-slag cylinders.....	22
9	Full size brick, 4.5x9 in. (115x230 mm), produced with dicalcium silicate slag and fillers.....	24
10	Concise equipment and materials flowsheet for producing brick from sand and waste slag by steam autoclave process.....	26

INTRODUCTION

The Canada Centre for Mineral and Energy Technology, (CANMET), of the Department of Energy, Mines and Resources is conducting research on the economic recovery of useful minerals, metals and products from the large buildup of solid wastes from mining and metallurgical processing. A large proportion of solid metallurgical wastes is slags, which are usually solid solutions of various metallic silicates. Iron blast-furnace slag may be used for the manufacture of Portland cement, as concrete aggregate, or as railroad ballast. Most non-ferrous smelting slags are discarded as worthless, although some are processed for their metallic content.

A unique slag which currently is being discarded is the dicalcium silicate slag produced at the Haley Station, Ontario, magnesium plant by the vacuum reduction of calcined dolomite with ferrosilicon at 1200°C. About one million tons of this finely divided, powdery material have been produced. It has been observed to set up, or form a weak bond in the slag pile. Some use has been made of this material as a roadside or barnyard fill, but with little economic benefit to the company. CANMET agreed to undertake an investigation aimed at developing a use for this waste product so that the company's revenue could be augmented and the viability of the magnesium production facility could be ensured.

THE SLAG

The slag used in this investigation originated at the magnesium works of Chromasco Corporation at Haley Station, Ontario. The hot slag

in briquet form, is normally air-conveyed from the reduction area of the plant and water-quenched in the plant yard. Upon cooling, the slag breaks down to a fine material that is trucked to the slag dump. A 275-pound (125-kilogram) sample of dry, air-cooled slag was obtained from the company.

Approximately 95 per cent of the slag produced is calcium orthosilicate, Ca_2SiO_4. Dicalcium silicate can exist in three main forms-

$$\alpha\text{-}Ca_2SiO_4 \overset{1420^{\circ}C}{\rightleftharpoons} \beta\text{-}Ca_2SiO_4 \overset{675^{\circ}C}{\rightleftharpoons} \gamma\text{-}Ca_2SiO_4$$

The transition from the β- to the γ- form on cooling is attended by an expansion of about 10 per cent, which shatters the slag into a fine dust. This phenomenon, known as decrepitation or dusting [1], has been observed in orthosilicate-containing slags.

Tables 1 and 2 give screen and chemical analyses of the slag as received. It is noteworthy that the largest portion of unreacted MgO is in the coarsest fraction, and also that an air-cooled slag is much finer. The small amount of fluorine detected is derived from the 2.5 weight per cent of fluorspar added to the reduction mix. Table 3 shows X-ray qualitative analyses which indicate that both β- and $\gamma\text{-}Ca_2SiO_4$ are present in roughly equal proportions.

Beta dicalcium silicate is known to be a major constituent of Portland cement clinker, and is described as belite or larnite, a product of imperfect crystallization or non-equilibrium composition [2]. Dicalcium silicate, with a lattice modified with traces of Al_2O_3 or Fe_2O_3, or with small amounts of B_2O_3, undergoes no β- to γ-transformation, and the persistent β-phase is generally considered to be hydraulic. However, Korneev and Bygalina [3] have shown that $\beta\text{-}Ca_2SiO_4$, with ratios of $\frac{CaO}{SiO_2} \leq 2$,

TABLE 1

Sieve Analyses of Dicalcium Silicate Slag, Wt Per Cent

Mesh Size	Water Quenched	Air Cooled
+10	23.1	3.3
-10 +20	13.8	1.3
-20 +48	22.6	6.9
-48 +100	15.4	6.3
-100 +200	9.5	14.7
-200 +325	6.0	15.9
-325	9.6	51.6
Total	100.0	100.0

TABLE 2

Chemical Analyses of Dicalcium Silicate Slag Fractions (Air Cooled) - Wt Per Cent

Ingredient	+10 mesh	-10 + 325 mesh	-325 mesh	As Rec'd
CaO	57.9	60.9	62.1	61.4
MgO	11.7	1.4	1.2	1.6
SiO_2	26.1	33.2	34.0	33.4
Fe_2O_3	3.4	3.0	2.4	2.7
Al_2O_3	0.62	1.3	0.30	0.76
R_2O_3	4.1	4.3	2.7	3.4
P^2O_3	0.87	0.75	0.52	0.64
Molar Ratio CaO/SiO_2	2.30	1.97	1.96	1.97

TABLE 3

Qualitative X-ray Analyses of Dicalcium Silicate Slag

Slag	Major Components	Minor Components
Water Quenched	β- and γ-Ca_2SiO_4	MgO
Air Cooled	β- and γ-Ca_2SiO_4	MgO, SiC

TABLE 4

Hydraulic Activity of 50% Slag (-100 mesh), 50% Silica (-200 mesh) Mixture Pressed at 5000 psi (34 MPa)* with 15% moisture, cured in a humid atmosphere at 70°F(21°C)

Time Days	Compressive Strength	
	psi	MPa
0	140	1.0
8	260	2.0
8 (dry air)	130	0.9
28	460	3.2

*Pa= Pascal, metric unit for stress; 1 psi = 6.89 KPa

has little hydraulic activity; it does not readily form a hydrate in a moist environment at room temperature (25°C) or in a steam autoclave (150°C). The Chromasco slag has a ratio of $\frac{CaO}{SiO_2}$ <2 (1.97) and tests with 1.74-in. (44-mm) diameter cylinders (Table 4) indicate that the hydraulic activity is indeed small.

Other properties of the slag are shown in Table 5. The physical properties, such as bulk density, specific gravity and surface area, change with exposure to water at room temperature and to steam in an autoclave, indicating possible hydration of the slag components. Figure 1 shows weight loss of the slag, as received, and after autoclaving, when heated in a Stanton thermobalance. The as-received material shows only weight gain above 1470°F (800°C), which is attributed to the oxidation of residual ferrosilicon. In the case of autoclaved slags, sharp weight losses were observed at temperatures corresponding to the decomposition of $Mg(OH)_2$. The weight loss for the sample autoclaved at 200°C (392°F) was 4.7 per cent, about eight times the weight loss that would be expected from the hydration of all of the free MgO present; a Ca_2SiO_4 hydrate is indicated to have formed in the autoclave.

Speakman and Taylor [4] have shown that a reaction occurs in suspensions or slurries of γ-Ca_2SiO_4 under saturated steam pressure at temperatures above 150°C (303°F). They have described the resulting phase as either a mixture of calciochondrite and kilochoanite ($Ca_3Si_2O_7$ approx), or γ-Ca_2SiO_4 "hydrate". These scientists found that autoclaved blocks with strengths of up to 10,000 psi (69 MPa) could be obtained by autoclaving dry-pressed blocks of γ-Ca_2SiO_4 either alone or mixed with finely divided quartz.

TABLE 5

Miscellaneous Properties of Dicalcium Silicate Slag

1. Bulk Density (-20 mesh)	lb/ft^3	g/cm^3
Air cooled, as received	65.0	1.04
Water cooled, as received	55.6	0.89
Air cooled, autoclaved*	33.3	0.53
2. Specific Gravity (-20 mesh)		
Air cooled, as received	3.13	
Water cooled, as received	3.08	
Air cooled, autoclaved*	2.82	
Theoretical, Ca_2SiO_4	3.28	
3. Surface Area (-20 mesh)	m^2/g	
Air cooled, as received	1.12	
Water cooled, as received	9.06	
Air cooled, water slurried 24 hours	3.17	
Air cooled, autoclaved*	4.03	
4. Acid Consumption (to pH3) $CaCO_3$ equivalent		
	HCl	H_2SO_4
Air cooled, -20 mesh	0.82	0.81
Air cooled, -100 mesh	0.91	0.91
Water cooled, -20 mesh	0.61	0.59

*Autoclaved in steam for 24 hours at 50 psig (0.37 MPa) and 298°F (148°C)

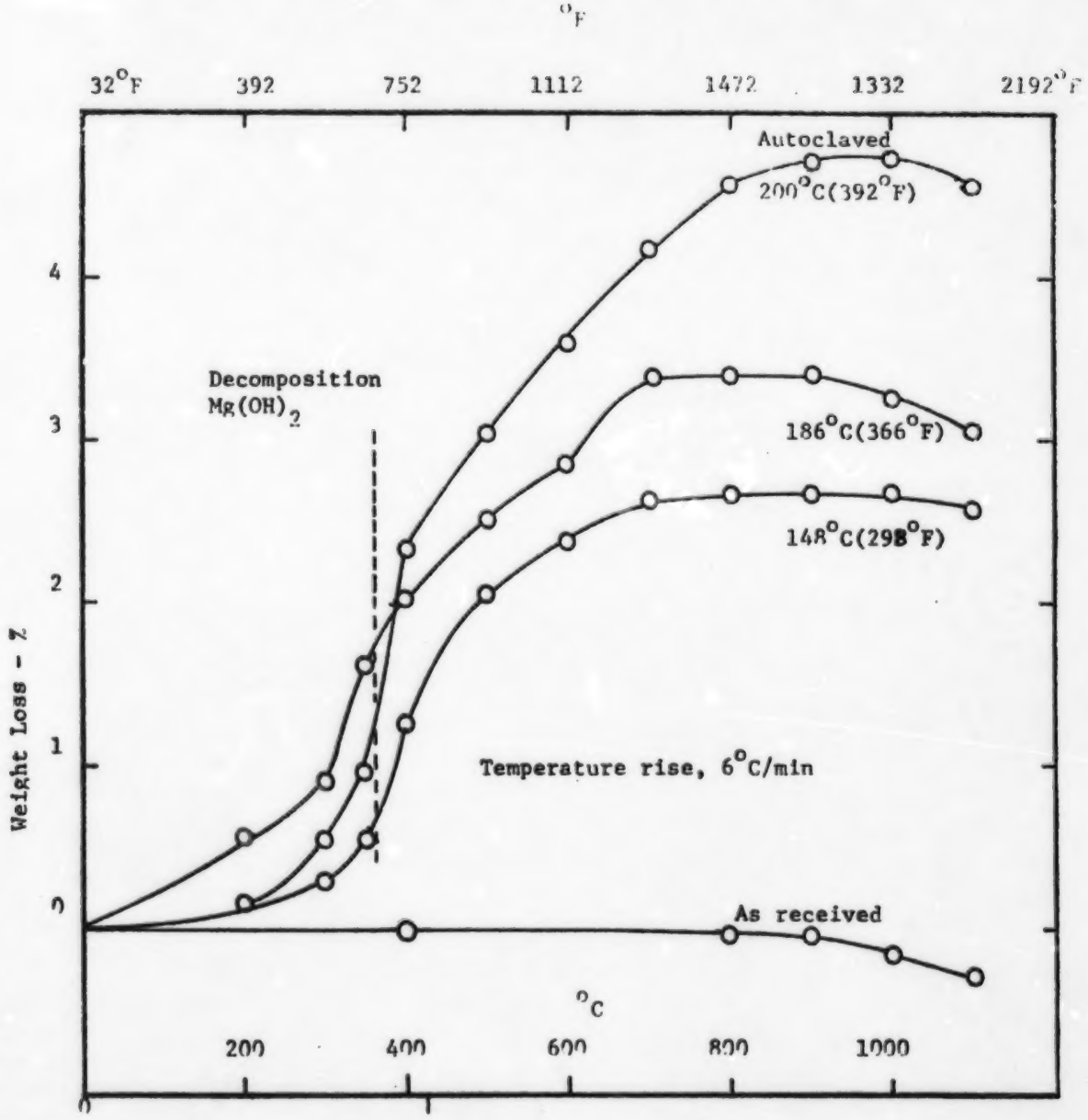

Figure 1. Weight loss vs temperature for minus 100-mesh dicalcium silicate slag, as received, and after autoclaving for 24 hours.

Initial attempts to produce an autoclaved block with the slag in the Mineral Sciences laboratories were not successful. Dry-pressed slag cylinders expanded about 20 per cent and showed no significant strength upon autoclaving, probably due to residual MgO which expands about 10 per cent on hydration. This effect of residual MgO could be negated by removal of most of the MgO by screening or by hydration to $Mg(OH)_2$.

Ultimately, autoclaved blocks and cylinders with individual compressive strengths as high as 13,000 psi (90 MPa) were manufactured by first hydrating the MgO at 298°F (148°C) in a thick slurry or in a steam autoclave, and then autoclaving a dry-pressed shape of slag alone or in mixtures with graded silica, dolomite or sand.

Other properties and possible uses of the slag were investigated, such as conversion to a hydraulic Portland-type cement, but with negative results, as shown in Appendix I. The utilization of the waste slag in agriculture was also examined (Appendix II) but the results were not promising.

THE MANUFACTURE OF AUTOCLAVED BLOCKS WITH WASTE DICALCIUM SILICATE SLAG

Hydration of Residual Magnesia

Because the reduction of calcined dolomite in the Pidgeon process is incomplete in spite of a stoichiometric excess of silicon, unreacted dolomite could be present. X-ray diffraction identified MgO in the slag, as shown in Table 3. The largest concentration of MgO is found in the coarser fractions (Table 2); therefore, the MgO content may be substantially reduced by screening.

Figure 2 shows the minus 100-mesh fraction after pressing at 5000 psi (35 MPa) and also after autoclaving, indicating that the reduction of magnesia content is insufficient. Autoclave environments led to expansion.

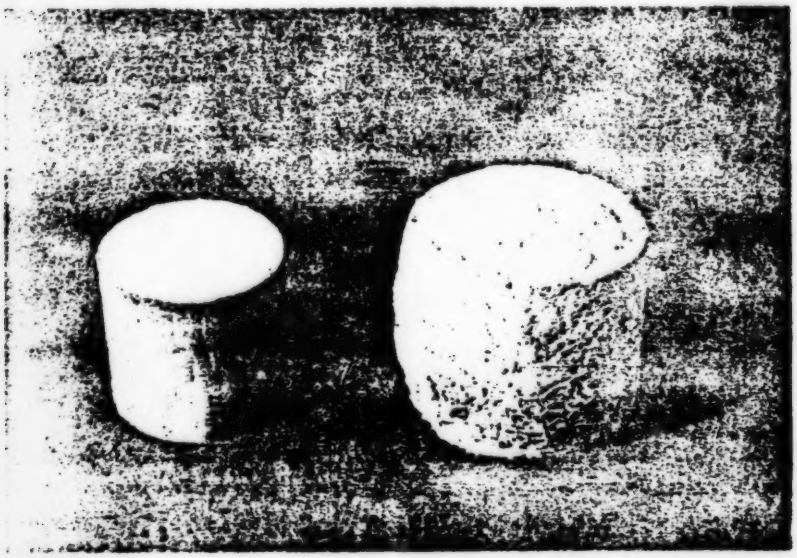

Figure 2. Slag cylinders formed with minus 100-mesh material (left) and (right) after autoclaving at 392°F (200°C)

In order to hydrate the residual magnesia, three methods were attempted: a) hydration in a hot slurry, i.e., below 203°F (95°C); b) hydration as a moist powder in an autoclave at low pressure, e.g., 50 psig (0.34 MPa), and c) hydration as a thick slurry in a stirring autoclave

at low pressure, e.g., 50 psig (0.34 MPa). Tables 6 to 8 show the results obtained by these three methods. The degree of "hydration" of the magnesia fraction was determined by pressing a sample of the hydrated slag containing 8 per cent water at 5000 psi (34 MPa) and autoclaving for a few hours at 200 psig (1.4 MPa). Each autoclaved specimen was examined for cracking or surface spalling, associated with expansion during hydration of the magnesia.

TABLE 6

Hydration of Slag as Thick Slurry at 194°F (90°C) (60% solids)

Mesh Size	Slurry Mix Time (hours)	Filter-ability	Autoclaved Specimen Condition
- 20	17	poor	disintegrated
-100	18	poor	disintegrated
-100	20*	poor	disintegrated

* Slurried in a 2 molar solution of Na_2CO_3

TABLE 7

Hydration of Slag as Moist Powder in an Autoclave

Mesh Size	Hydration Conditions			Autoclaved Specimen Condition*
	°F	°C	Psig	
- 20	266	148	50	5
- 35	"	"	"	4
- 65	"	"	"	2
-100	"	"	"	0
- 20	338	170	100	3
- 35	"	"	"	2
- 65	"	"	"	1
-100	"	"	"	0
- 20	367	186	150	2
- 35	"	"	"	1
- 65	"	"	"	0
-100	"	"	"	0
- 20	388	198	200	1
- 35	"	"	"	1
- 65	"	"	"	0
-100	"	"	"	0

* 5 Specimen completely disintegrated
4 Specimen partly disintegrated
3 Surface disintegrated
2 Slight surface spalling
1 Very slight surface spalling
0 Specimen in excellent condition

TABLE 8

Hydration of Slag as a Thick Slurry under Pressure
50 Per Cent Solids, 50 psig (0.34 MPa)

Mesh Size	Time hours	Slurry Filterability Imp gal/hr/ft^2*	Autoclaved Specimen Condition**
- 35	1	8.1	5
	3	3.2	3
	6	3.0	1
	12	3.5	0
- 48	1	N.D.***	0
	3	N.D.	0
- 65	1	3.9	1
	3	3.5	0
	6	4.2	0
	12	2.8	0
-100	1	4.7	0
	3	11.3	0
	12	N.D.	0

* Imp gal/hr/ft^2 - 1 liter/hour/meter^2. Filtration tests were performed with a laboratory Buchner funnel with Whatman number 1 filter paper. The filter cake was allowed to build up to 1 in. (2.5 cm) thickness under 15 in. (38 cm) mercury of vacuum. The filter cake averaged 16.5 per cent moisture.

** 1.74 in. (44 mm) cylinders were pressed with 50 per cent sand at 5000 psi (34 MPa), 8 per cent water, and autoclaved for 2 hours at 150 psig (1.0 MPa)

*** N.D. - not determined.

As shown in Table 6, hot slurries of the slag at atmospheric pressure gave unsatisfactory results. Specimens pressed from the filtered and dried material broke up on autoclaving. Also, the hot slurry was difficult to filter. Table 7 shows the effect of various autoclave treatments of moist slag on the hydration of the magnesia component. Specimens pressed from the autoclaved slag and again autoclaved were examined.

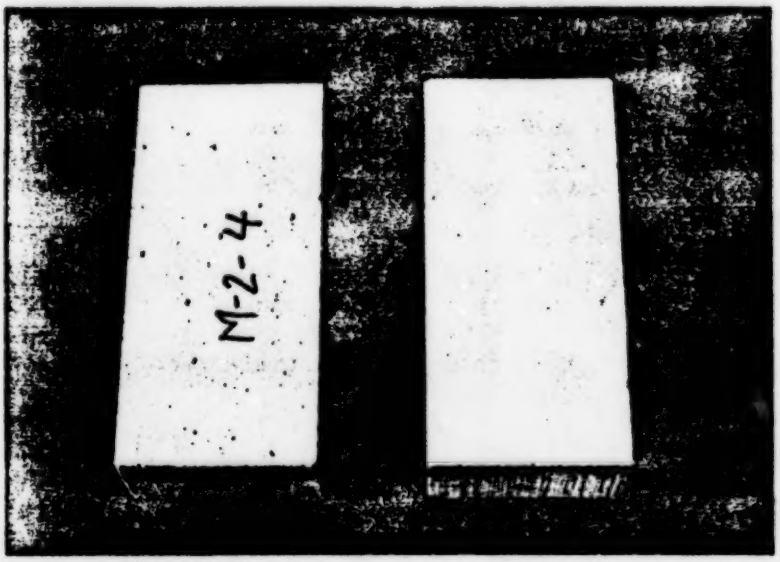

Figure 3. "Half" bricks made from slag; magnesia incompletely hydrated (left) and completely hydrated (right).

The extent of the damage caused by hydration expansion was rated numerically from 5 (total disintegration) to 0 (acceptable, no visible defects). Specimens formed with minus 100-mesh material were acceptable after autoclaving at 50 psig (0.34 MPa); however, those formed with minus 20-mesh material showed surface defects, even when the autoclaving pressure was increased to 200 psig (1.4 MPa). Figure 3 shows surface defects, or pits, produced when the magnesia is incompletely hydrated. At the centre of each surface pit was a powdery white material identified as magnesium hydroxide.

Table 8 shows the results of hydration tests in a low-pressure stirring autoclave. The results were generally superior to those obtained using moist powder. Only three hours were required to autoclave minus 65-mesh material, while substantially longer times and increased pressures were required for the moist form.

Because of the difficulty in processing the dry slag on an industrial scale, the slurry method would be preferred. However, equipment limitations in the laboratory led to the hydration of the slag by moistening the minus 100-mesh fraction with 8 per cent water and autoclaving in 25-pound batches for 24 hours at 50 psig (0.34 MPa).

It was noted that severe corrosion of the brass and copper fittings on the autoclaves occurred during the hydration step. At first thought to be fluoride corrosion, this was later determined to be ammonia corrosion. The air-cooled slag, when moistened, gave off a pungent, unpleasant odor, probably a combination of ammonia and hydrocarbons resulting from the decomposition of metallic nitrides and carbides, e.g., magnesium nitride which decomposes in the presence of water-

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3 \text{ (gas)}$$

The magnesium nitride content of the slag, as received, was determined by distillation to be 0.34 per cent Mg_3N_2 and 0.26 per cent Mg_3N_2 in the minus 100-mesh fraction.

Figure 1 shows that the slag reacted with water at autoclaving pressures above 50 psig (0.34 MPa). Figure 4 shows the change of surface area of the slag with autoclaving. A large increase in surface area below 50 psig (0.34 MPa) is associated with magnesium hydroxide formation, and a decrease in surface area is associated with hydration of the slag above that pressure. Figure 5 shows the slight increase in particle size resulting from autoclaving at low pressure.

Fabrication of Brick

A. Pressing

Three sizes of "brick" were made in the laboratory; cylinders 1.74 in. (44 mm) in diameter; half brick, 2.88 in. by 6.0 in. (73 x 153 mm); and full-size brick, 4.5 in. by 9.0 in. (115 x 230 mm). An air-operated, 50-ton capacity Hydrolair press was used to press the cylinders, a 100-ton mechanical Tinius-Olsen press for the half bricks, and a 225-ton hydraulic Farguhar press for the full-size bricks. Pressing force was applied top and bottom in each case. The half-brick press was difficult to operate and the moulds were poor so only a few bricks were made of this size. The applied pressure was usually 5000 psi (34 MPa). Moisture contents of 8 and 10 per cent by weight in the green brick gave the best results.

B. Autoclave Procedure

Two sizes of steam autoclaves were employed, a 6-inch diameter, 0.23-cubic foot, top-loading, 450-psig capacity autoclave, and a 2-foot diameter, 16-cubic foot, 150-psig capacity, end-loading, autoclave.

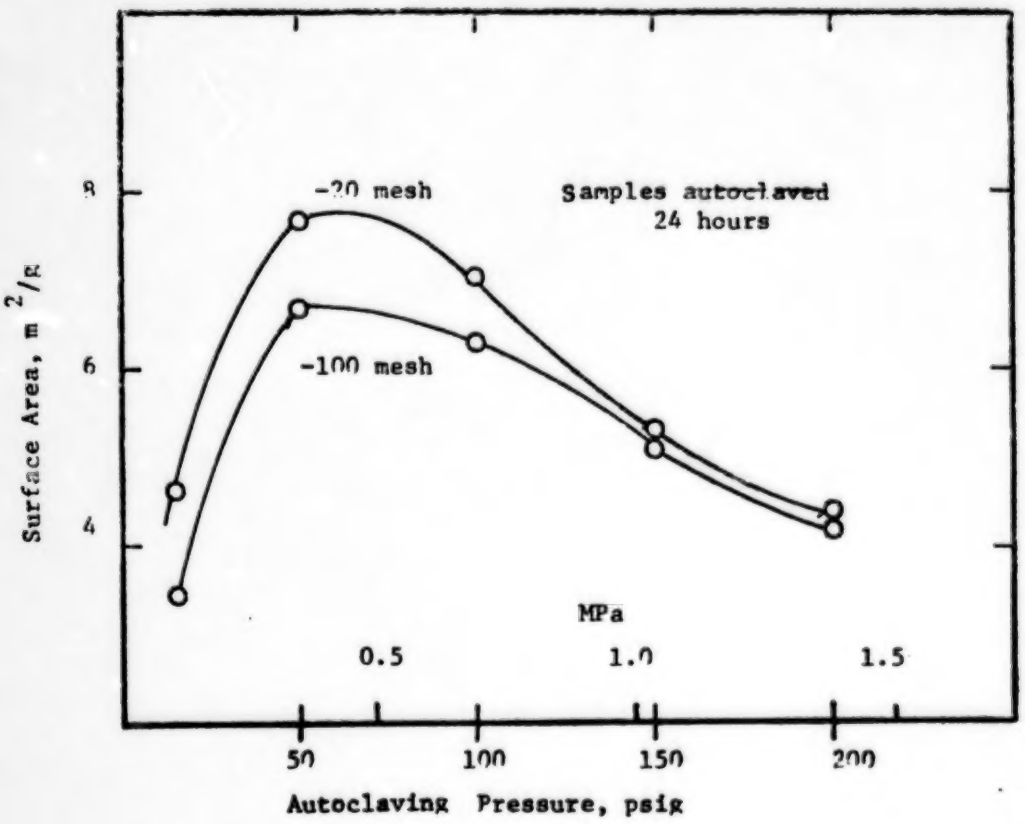

Figure 4. Change of surface area with autoclaving of screened slag.

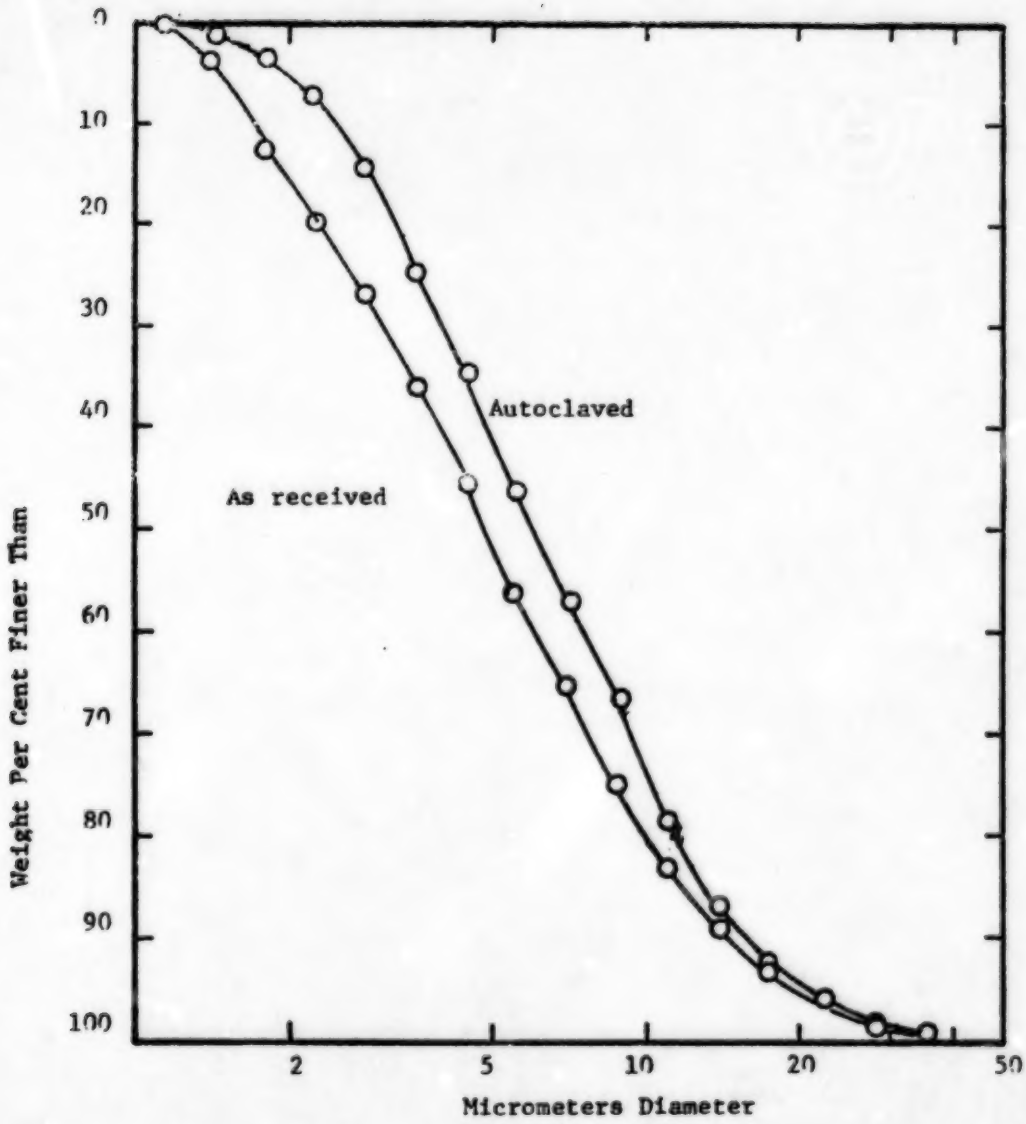

Figure 5. Fine particle size analyses of minus 200-mesh slag as received and autoclaved 24 hours at 50 psig (0.34 MPa).

both units were heated and pressurized by electrically heated water wells at the bottom. Green specimens were protected from dripping water in the autoclave by an aluminum foil or a metal sheet cover. Two hours heat-up time was required, air being bled from the autoclaves during the heat-up period.

C. Specimen Testing

Autoclaved products were tested in accordance with ASTM C67, "Sampling and Testing of Brick". Rather than test full-size brick, in some instances, 2-inch cubes sawn from the large bricks were used.

Results

A. Moulding Pressure and Autoclaving Time

Figure 6 shows the compressive strengths of small cylinders, which had been pressed from hydrated minus 100-mesh slag and 10 per cent water, and autoclaved for various times at 100 psig (0.69 MPa). Higher forming pressures and longer autoclaving times were generally beneficial. However, some loss in compressive strengths was observed after 48 hours, as has been noted by other scientists, [4,5,6]. No satisfactory explanation, other than the possibility of a disruptive phase formation, has been put forward.

B. Filler Additions

Autoclaved blocks with compressive strengths as high as 10,900 psi (75 MPa) have been formed by other researchers by adding fine quartz to γ-dicalcium silicate, much greater than that achieved by using γ-dicalcium silicate alone. Figure 7 shows the effect of various "fillers", e.g., crushed quartz, natural sand and crushed dolomite, on compressive strength of autoclaved cylinders. The screen analyses of these materials are shown in

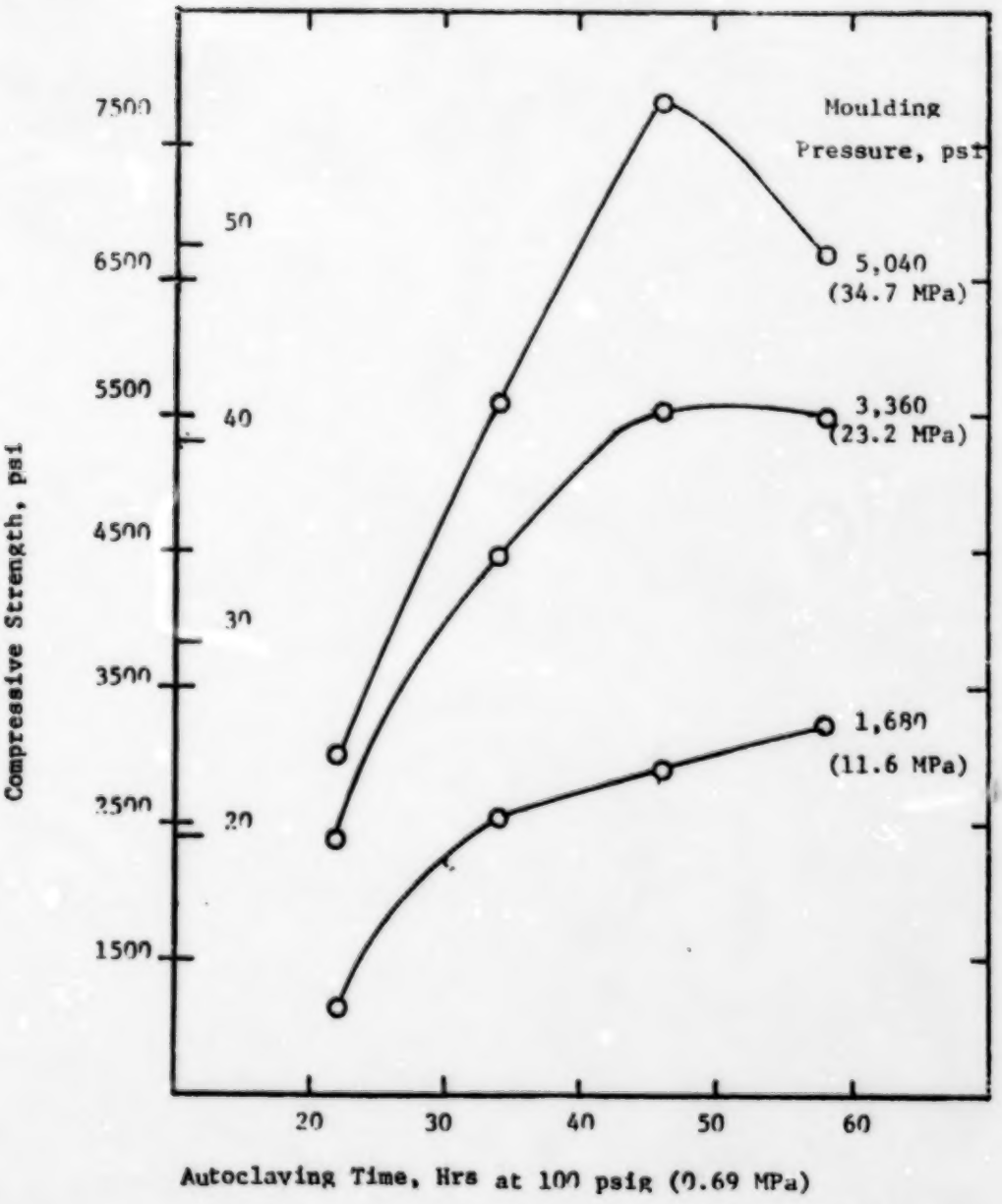

Figure 6. Effect of moulding pressure and autoclaving time on compressive strength of slag cylinders.

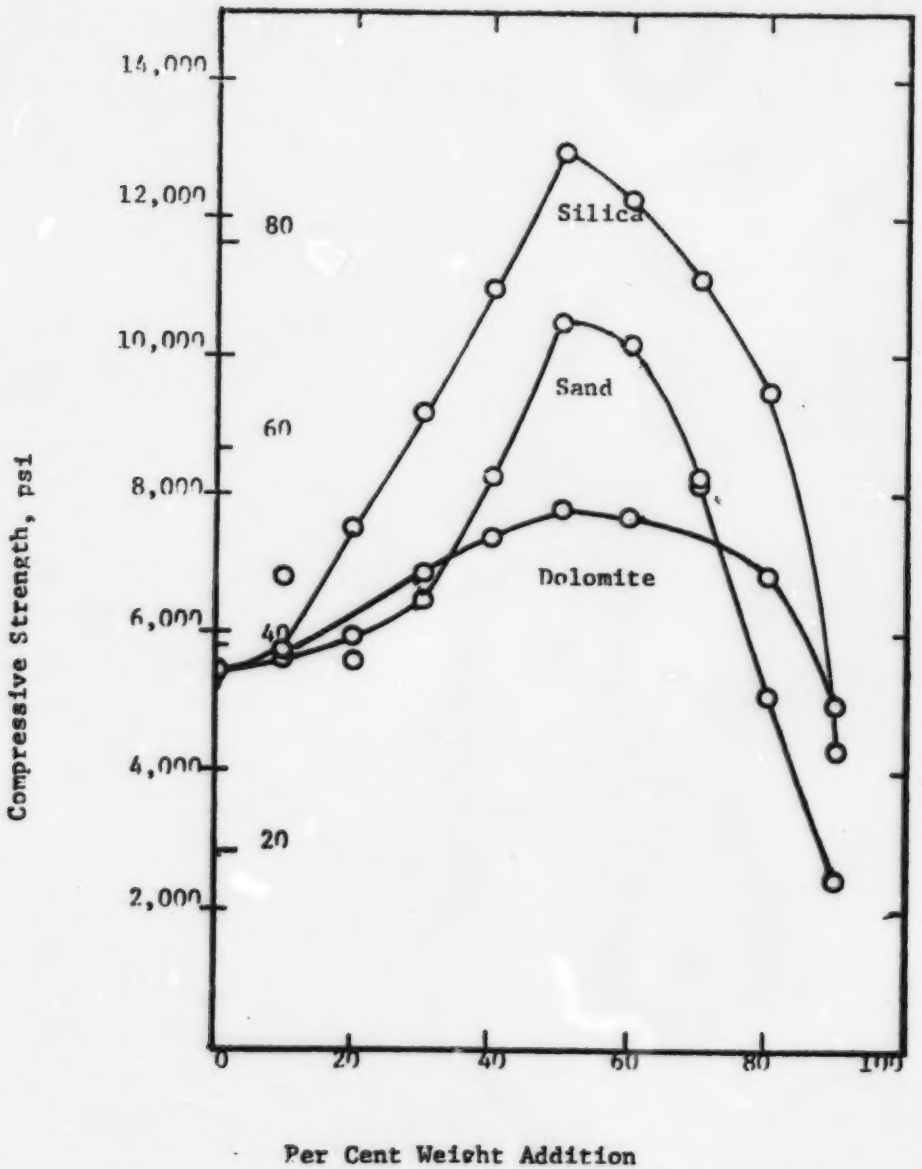

Figure 7. Effect of various fillers on the compressive strength of slag cylinders autoclaved for 48 hrs at 100 psig (0.69 MPa).

Appendix III. The addition of each filler considerably improved the moulding operation. Additions of 50 weight per cent of each filler gave the highest compressive strengths. It was apparent that the higher strength achieved with silica was because of silica-slag reaction as determined by other researchers, [4,7], where the formation of tobermorite, ($5CaO.6SiO_2.5H_2O$) was reported.

C. Autoclave Pressure and Time

Autoclaved products such as sand-lime brick and concrete products, normally are subjected to pressures as high as 200 psig (1.4 MPa). Figure 8 shows the effect of various pressures and times on the compressive strength of sand-slag cylinders (50 weight per cent each). Increasing autoclaving pressure from 100 to 150 psig (0.69 to 1.0 MPa) decreases the time required to develop strengths of 6000 psi (41 MPa) from 48 to 12 hours. Increasing pressure from 150 to 200 psig (1.0 to 1.4 MPa) does not appear to be as significant.

D. Standard Tests

Twelve full-size bricks were made from each of slag alone and slag mixed with sand, and six were made from each of slag-dolomite and slag-silica mixtures as shown in Table 9. Tests were performed on these bricks as closely as possible in accordance with ASTM C67, "Sampling and Testing of Brick". No shrinkage or warpage was measureable in any of the bricks, and no efflorescence was formed by half submerging samples of each for 24 hours.

The bricks made from slag alone did not meet the specifications for clay facing-brick, but exceeded those for sand-lime brick. Fifty weight per cent additions of fillers gave products that met both specifications, although the saturation coefficients (C/B ratios) exceeded the desired levels for facing masonry exposed to the weather. However, this requirement

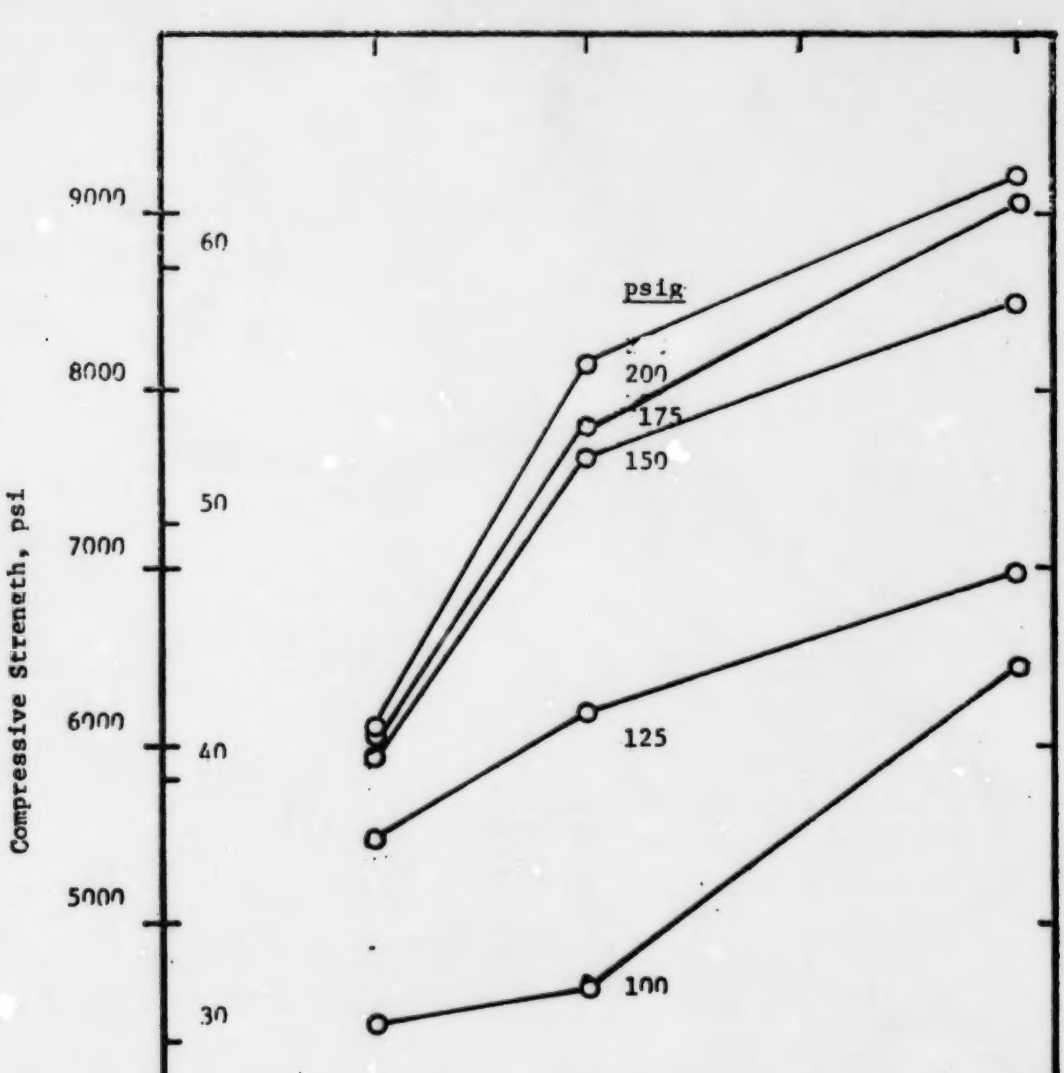

Figure 8. Effect of autoclaving time and pressure on the compressive strength of sand-slag cylinders.

TABLE 9

Summary of Slag Brick Properties*

Composition	Brick Forming Conditions								Brick Properties								Freeze-Thaw	Initial Rate of Absorption
	Autoclave I			Pressing Press		Autoclave II			Bulk Density	Compressive Strength		Modulus of Rupture		Water Absorption				
	hrs	psig	MPa	psi	MPa	hrs	psig	MPa	g/cc	psi	MPa	psi	MPa	COLD	HOT	C/B	Cycles to Failure	gm/30 in²
Slag -100 M	24	50	(0.34)	5000	(34)	48	100	(0.69)	1.73	7080	(48.8)	1350	(9.3)	20.4	22.4	0.91	42	19.3
Slag -100 M Natural Sand	"	"	"	"	"	"	"	"	1.95	9860	(67.9)	1046	(7.2)	12.0	13.6	0.88	50+	4.1
Slag - 100 M Dolomite	"	"	"	"	"	"	"	"	1.99	8430	(58.1)	970	(6.7)	12.7	14.5	0.88	50+	7.3
Slag -100 M Quartz -8 M	"	"	"	"	"	"	"	"	1.89	9740	(67.1)	1110	(7.6)	13.9	15.1	0.92	50+	4.8
Lime Brick Specification										4500 min	(31)	600 min	(4.1)		20 max			5 max
Brick Specification										3000 min	(21)			17.0 min	20.0	0.78 max	50+ min	4-15 22 max
															or			
										8000	(76)	either		8 max		0.88 or greater	50+ min	
Total									4	8		7		2	2		8	7

* Tested in accordance with ASTM C67

was waived because these bricks exceeded the stimulated compressive strength value of 8,000 psi (55 MPa) and they surpassed the specified 50 cycles in the test for resistance to freezing and thawing.

The autoclaved product had a light grey surface and a high degree of mechanical perfection as shown in Figure 9. Insufficient mine-tailings material was available to include in the testing program, but indications were that the slag-mine tailings brick had properties similar to the slag-sand brick.

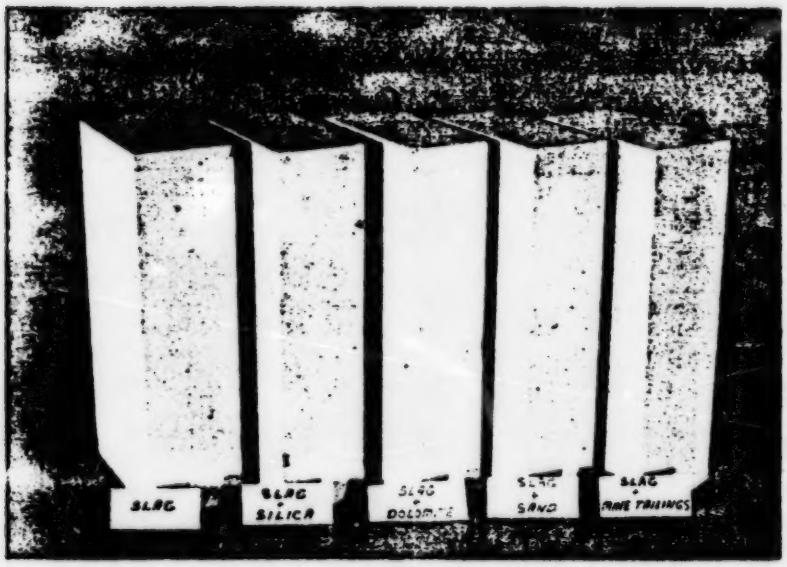

Figure 9. Full size brick, 4.5 x 9 in. (115 x 230 mm), produced with dicalcium silicate slag and fillers.

Economics of Brick Production

An economic evaluation of the production of bricks from sand and slag was prepared on the basis of a production of 20 million, 4.5 pound bricks per year. The operating year was assumed to be 250 days at 24 hours per day. Equipment costs were derived using an assumed 1974 Marshall and Steven's Index of 450, compared to a mid-1971 index of 321, and using published data for similar equipment, [8,9,10,11,12]. Plant depreciation is assumed to be linear over a 7 year life.

A concise flowsheet is shown in Figure 10, and the estimated capital cost is shown in Table 10. The operating cost per 1,000 bricks, as shown in Table 11, was estimated to be $53.14. The estimated shipping cost, based on a quoted rate of $0.49 per hundred weight for a 250 mile distance, would be $22.05 per 1,000, bringing the anticipated cost of delivery to market of $75.19 per 1,000 bricks. The anticipated market value could be little more than that for sand-lime bricks, approximately $75.00.

It is apparent that a commercial operation producing bricks from this slag would not be profitable at this time.

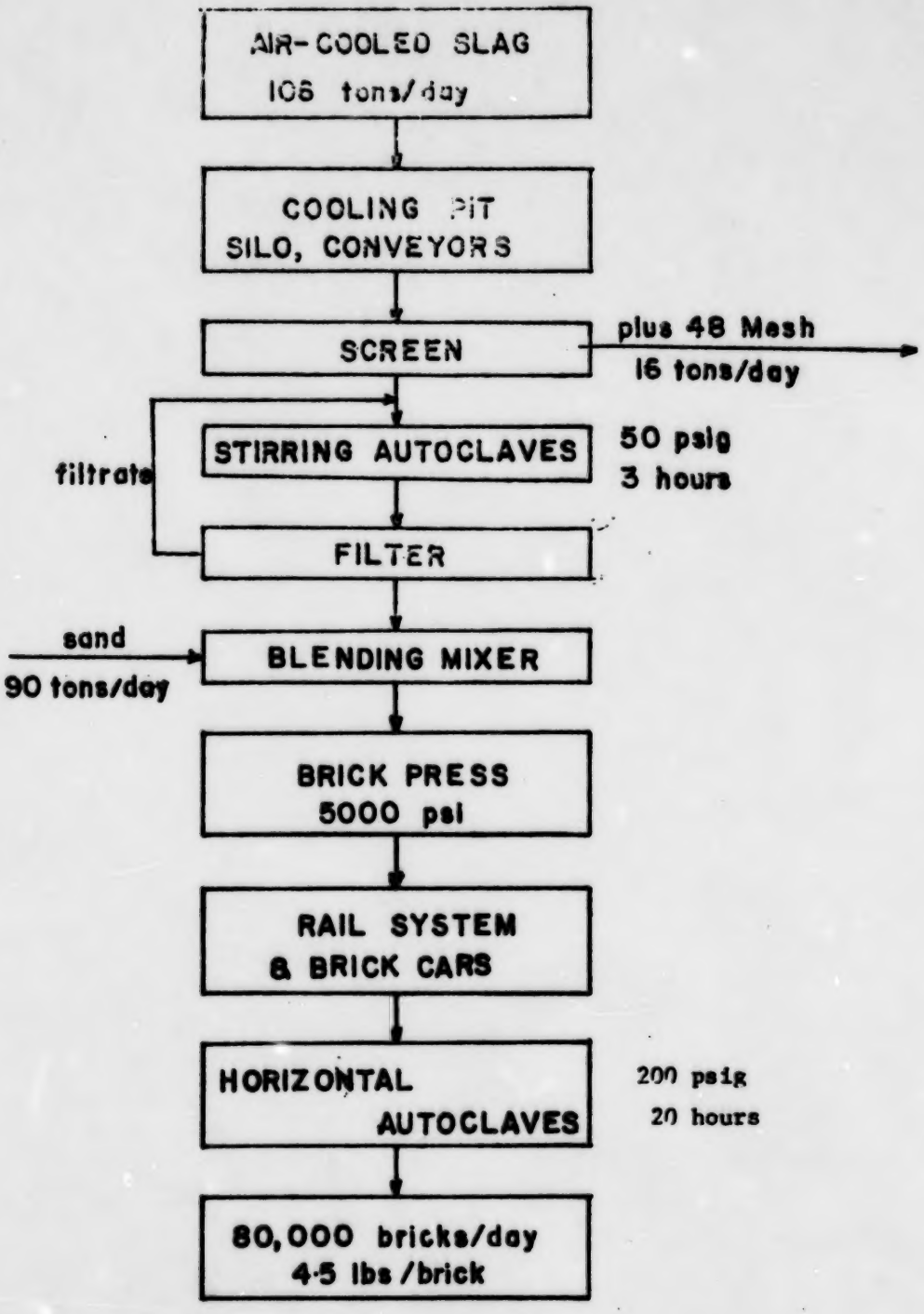

Figure 10. Concise equipment and materials flowsheet for producing brick from sand and waste slag by steam autoclave process.

TABLE 10

Estimated Capital Cost for Brick Production

Dry material handling equipment	$85,000
Screen	6,300
Stirring autoclaves	29,100
Fitters and pumps	44,100
Mixing and blending equipment	24,600
Brick press	121,400
Brick cars and rail system	65,000
Horizontal autoclaves	312,000
Steam boiler	78,500
Dust and fume collectors	7,600
Weightometer	5,600
Mobile equipment	32,800
Total equipment capital cost	$812,000
Equipment cost X factor	
Foundations X 0.3	
Buildings X 0.2	
Structures X 0.1	
Electrical X 0.02	
Miscellaneous X 0.05	
Total factor 0.67	544,000
Total direct cost	1,356,000
Field indirect, 10 per cent of total cost	135,600
Total construction cost	1,491,600
Engineering, 5 per cent of construction cost	74,500
Administration and overhead, 5 per cent of construction cost	74,500
Sub-total	1,640,600
Contingency, 10 per cent of sub-total	164,100
Contractor's Fee, 5 per cent of sub-total	82,100
Total Fixed Capital Cost	$1,886,800

TABLE 11

Estimated Manufacturing Cost per 1,000 Bricks

Raw Materials	
Dry slag	$0
Sand, dry, at $2.50 per ton	2.81
Sand, trucking, 15 miles at $0.75 per ton	.84
Process water, at $0.25 per 1000 gallons	.08
Total raw materials	3.73
Direct Costs	
Labour, at $5.50 per hour	15.44
Supervisory cost	2.30
Plant maintenance	2.27
Plant overhead (0.3 x labour)	4.63
Operating supplies	.46
Power at $0.02 per kwhr	.42
Natural gas at $1.00 per million BTU	1.35
Total direct costs	26.87
Indirect Costs	
Administration and overhead (0.3 x direct costs)	8.06
Taxes and insurance	1.00
Depreciation, 7 years	13.48
Total indirect costs	22.54
Total Cost per 1,000 Bricks	$53.14

Conclusions

Good quality building bricks were produced by utilizing the high temperature hydration properties of waste dicalcium silicate slag. Fabrication of these bricks was made considerably more complex and expensive because of the presence of small amounts of free magnesium oxide in the slag. A cost analysis has shown that production costs would exceed expected market value, thus this novel building material would not be competitive with other readily available materials.

In the future, however, accumulations of these waste slags could be utilized for the production of building materials as the more conventional energy-intensive materials, such as Portland cement, lime and clay products, become more expensive.

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APPENDIX I

The Manufacture of Hydraulic Cement from Dicalcium Silicate Slag

A Stabilization of Ca_2SiO_4 in β-Form

Dicalcium silicate exists in several forms, the interrelationship of which is not completely understood nor agreed upon. Five distinct polymorphs have been identified: α, α', β, β' and γ. Of concern to this study are the β and γ forms. The β→γ transformation takes place on cooling at about 675°C (1250°F), and the monoclinic (β) form, density 3.28, expands to the orthorhombic (γ), density 2.97, usually causing decrepitation of the material. The β form is a major constituent of Portland cement and slag cements, and forms a hydrate. It has long been recognised that the β form can be stabilized at room temperature by additives such as B_2O_3 [1,2]. More recent investigators, [3], found that a wide range of additives, either singly or in combination, and fired with stoichiometric dicalcium silicate, produced the hydraulically active β form. Table I shows the results of firing the Haley slag pelletized with various additives, at 2550°F (1400°C) for one hour in chromite crucibles. A gas-fired Remmy furnace was used and the samples were allowed to cool outside the furnace. Only samples 1 and 7 decrepitated on cooling, the remainder appearing to be stabilized in the higher temperature form. However, X-ray diffraction analyses revealed that only samples 3 to 6 were devoid of the lower temperature γ form. Of these, only sample 3, "stabilized" with 3 mol per cent each of Cr_2O_3 and Na_2CO_3, exhibited any indication of hydraulic activity, which in this case was slight, thus further investigations were not undertaken.

TABLE I

Dicalcium Silicate Stabilized By Various Additives

	Specimen	Forms Identified by X-ray Diffraction	Hydraulic Activity*
1	Ca_2SiO_4 (slag)	$\beta + \gamma$	none
2	Slag + 3 mol % Cr_2O_3	$\beta + \gamma$	none
3	Slag + 3 mol % Cr_2O_3 + 3 mol % Na_2CO_3	$\alpha + \beta$	slight
4	Slag + 3 mol % V_2O_5	$\beta + \alpha$	none
5	Slag + 3 mol % V_2O_5 + 3 mol % Na_2CO_3	$\beta + \alpha$	none
6	Slag + 3 mol % H_3BO_3	$\beta + \alpha$	none
7	Slag + 3 mol % $Na_2H_2PO_4$	$\beta + \gamma + \alpha$	none
8	Slag + 3 mol % $Ba(OH)_2$	$\beta + \alpha + \gamma$	none

* Hydraulic activity was determined by pressing 0.39-in. (1.0-cm) diameter cylinder of each fired specimen at 5000 psi (34 MPa), 10% moisture, and storing for 8 days in a humid environment at room temperature. Specimens were examined for increase in compressive strength by scratching the surface.

5 The Use of Dicalcium Silicate Slag as a Raw Material for Portland-Type Cement Manufacture.

Normal Portland cement consists of three principal compounds- tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), and tricalcium aluminate ($Ca_3Al_2O_6$ - plus other compounds of lesser importance). Chromasco dicalcium silicate appeared to be non-hydraulic because of lime deficiency. Attempts were made to fire various mixtures with the dicalcium silicate slag as the main constituent ingredient and additives such as lime, silica, alumina, mill scale (iron oxide), and calcium aluminate slag, were proportioned to give the approximate composition of Portland cement. The calcium aluminate slag is another waste product of the Haley operation which results from the reduction of lime with aluminium to produce calcium metal. This slag is approximately equimolar in lime (CaO) and alumina (Al_2O_3) and has been identified as being composed of the following; $Ca_{12}Al_{14}O_{33}$, ($12CaO.7Al_2O_3$) and $Ca_3Al_2O_6$, ($3CaOAl_2O_3$). Severe reaction was experienced between the dicalcium silicate slag and alumina, magnesia, zirconia, and fire-clay refractories. Only chromite, or graphite under a reducing atmosphere,was satisfactory in containing the dicalcium silicate slag alone or in combination with the above mixtures. It was postulated that the refractory problem arose from reaction with fluoride impurities: fluorspar is added to the reduction mix at the rate of 2.5 weight per cent.

Attempts to produce a hydraulic Portland-type cement using the dicalcium silicate slag as the main basic ingredient were not successful.

The 10-gram batches fired at 2550°F (1400°C) for one-half hour either decrepitated on cooling ($\beta \rightarrow \gamma$ transformation on cooling), or the resulting solid pellet, which was ground to minus 200 mesh, exhibited no hydraulic activity.

Further work was not warranted since the probable costs involved in producing a hydraulic cement, if a successful method were found, would likely exceed that of commercially available cements.

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APPENDIX II

The Use of Dicalcium Silicate Slag in Agriculture

Metallurgical slags have been used as agricultural liming materials: (i) blast furnace slag, used mainly to neutralize soil acidity and to supply calcium and magnesium; (ii) open-hearth slag, used because of its high manganese content in addition to its liming effect; and (iii) basic slag, used mainly as a phosphorous fertilizer rather than as a liming material since it contains 5 to 10 per cent available phosphorous.

Chromasco slag could act as a soil neutralizer and as a supplier of calcium and magnesium, although the availability of magnesium present as MgO is probably higher than that of calcium. Tests undertaken by the Soil Research Institute, Agriculture Canada, Ottawa, are summmarized in Table I. Two successive crops of vernal alfalfa, which is sensitive to acid conditions, were grown in pots of Charlottetown fine sandy loam soil with an initial pH of 4.8, a soil similar in some respects to the sandy soils close to the source of the waste dicalcium silicate. The treatments were (a) control, (b) 6 tons calcium silicate per acre, (c) 6 tons calcium carbonate per acre, (d) 200 pounds P_2O_5 per acre, (e) 200 pounds P_2O_5 plus 6 tons calcium silicate per acre, and (f) 200 pounds P_2O_5 plus 6 tons calcium carbonate. Reagent-grade calcium carbonate and monobasic calcium phosphate were used. All pots received 200 pounds per acre K_2O as potassium chloride. The treatments were replicated four times except for treatment (a) which was conducted in duplicate. An acre was taken to be equivalent to 2 million pounds of soil.

The slag gave results similar to those obtained from calcium carbonate and considerably increased the yield of alfalfa when phosphorous was not added. There was no effect of liming material on yield when phosphorous was added. The soil pH values (after cropping) showed that the slag was effective as a liming material.

Attempts to pelletize the slag using a disc pellitizer were unsuccessful; the dry slag flows very poorly and the wet slag is very sticky. A method to pelletize or granulate the slag would have to be developed before the waste material could be utilized as a soil neutralizer.

It is probable that application of the slag would result in improper exchangeable (Ca/Mg) ratio, since the magnesium present is more readily soluble. Previous investigations [1,2,3], have shown that excessive soluble magnesium decreases yields of oats, barley and alfalfa. Also, since the slag contains fluorine in unknown form, plant and soil chemistry studies should be undertaken before the slag is applied to the soil.

The handling problems, the possible adverse soil and plant chemistry effects, and the fact that the demand for soil neutralizers is low in the waste source area (only 350 tons of limestone were used in Renfrew County in 1962), indicate it is unlikely that the slag would find economic use as a soil additive.

TABLE 1

Use of Waste Dicalcium Silicate Slag as Soil Neutralizer
Greenhouse Growth Vernal Alfalfa (Two crops)

Soil Treatment	Yield g/Pot	Soil pH
(a) Control	1.8	4.6
(b) Slag	6.9	7.3
(c) $CaCO_3$	6.1	7.1
(d) P_2O_5	8.4	4.9
(e) P_2O_5 + Slag	8.5	7.2
(f) P_2O_5 + $CaCO_2$	8.2	7.2

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APPENDIX III

Screen Analyses of Fillers Added to Slag for Bricks

Material	Quartz	Natural Sand	Dolomite	Mine Tailings
Mesh				
- 8 + 14	5.0		5.0	
-14 + 20	4.5		4.5	8.5 (+20)
-20 + 28	5.5	2.7	5.5	6.8
-28 + 35	9.0	5.2	9.0	7.3
-35 + 48	11.0	16.3	11.0	10.6
-48 + 65	16.5	34.3	16.5	12.6
-65 + 100	13.5	24.3	13.5	18.8
-100 + 150	11.5	}13.8	11.5	13.5
-150 + 200	7.5		7.5	9.9
-200	16.0	3.4	16.0	12.0
Source	Prepared from lump quartz, Buckingham, Quebec	Washed sand from Ottawa, Ontario, sand pit	Prepared from lump dolomite from Haley Stn., Ontario	Hilton Iron Mines tailings, Shawville, Quebec